⑥

Ullmann's Encyclopedia of Industrial Chemistry

Sixth, Completely Revised Edition

Volume 36

Textile Auxiliaries
to
Tin, Tin Alloys, and
Tin Compounds

ⓌWILEY-VCH

Table 10. World polyester fiber production

Year	Amount, 10^6 t			Percentage (without polyolefin) of	
	Total	Staple fiber	Filament	Total fiber production	Synthetic fiber production
1970	1.6	0.9	0.7	8	33
1980	5.1	3.0	2.1	17	48
1990	8.7	4.7	3.9	23	58
1992	8.3			21	58

increased attention [311]. The amount of dye residues remaining on materials subjected to the all-in drum dyeing process, which is still occasionally used in the stocking industry, is much greater than after package dyeing with intermediate rinsing. Thus, in the first case, the potential risk of skin damage is somewhat increased but disappears after the material has been washed.

7. Dyeing of Polyester Fibers

For information on polyester (PES) fibers, see → Fibers, 1. Survey, Chap. 8. (properties); → Fibers, 2. Structure (form, structure); → Fibers, 3. General Production Technology; → Fibers, 4. Synthetic Organic, Chap. 2. (chemistry and production). For properties, see also [312].

PES fiber is quantitatively the most important synthetic fiber (see Table 10). Its inexpensive production from petrochemical raw materials and excellent textile properties alone and in combination with natural fibers guarantee PES fibers universal applicability. Starting with tire cord, technical fabrics for tarpaulin and seat belts, carpeting, and furnishing fabrics, uses also include clothing, especially mixed with wool for suiting and trouser materials and mixed with cotton for shirts, raincoats, trousers, and casual wear. Pure PES fibers, especially in textured form, are employed in the knitwear sector.

PES fibers are hydrophobic, thus water-soluble dyes do not attach. In contrast, PES fibers can be dyed easily with water-insoluble, small molecular dyes originally developed for dyeing cellulose acetate. Since the preferred dyeing medium is an aqueous liquor, the poorly water-soluble dyes must be dispersed before application (→ Disperse Dyes).

7.1. General

7.1.1. Dyeing in Aqueous Liquor

Since the fundamental work of MEYER and KARTASCHOFF in 1925 [313] and the studies of VICKERSTAFF [314] in the beginning of the 1950s, a large number of studies have been published on the kinetics and thermodynamics of dyeing cellulose acetate and synthetic fibers with disperse dyes in aqueous dyebaths. For a survey, see [315, pp. 67, pp. 147]. Disperse dyes as well as acid and basic dyes must be molecularly dispersed in the dyebath; i.e., the dye must be dissolved in the aqueous bath before it can adsorb to the fiber surface and then diffuse into the fiber.

Thus, the form in which the disperse dye is present in the dye liquor is decisive for the dyeing process. The water solubility and rate of dissolution are influenced by many factors including [316–318]:

1) Temperature
2) Particle size
3) Crystal modification
4) Crystal growth
5) Melting behavior
6) Type of dispersion and dispersing agent used (fineness, stability, agglomeration, aggregation of dispersion)
7) Presence of salts
8) Behavior in dye mixtures

The water solubility of pure disperse dyes is a few milligrams per liter and increases strongly with temperature. It is also increased manifold by dispersing agents [316, 319].

The state of the dye in the fiber is often compared to a solid solution. Thus, the thermodynamic dyeing equilibrium of a disperse dye between water and fiber follows the Nernst distribution law:

$$\left(\frac{C_F}{C_L}\right)_{t=\infty} = K$$

At constant t
ficient K [i.e.
dye dissolvec
(C_L) at equili

At norma
dissolution o
is assumed t
as long as un
not always v
liquor is also
molecularly c
to the fiber su
adsorption of
sion in the fi
rate of dyeing
in a certain ti

$$g = -\frac{D}{h} \cdot (C_1$$

The diffusi
10^{-12} cm^2/s
increase in to
predetermine
tion gradient

Many ex
velop an eq
However, on
the complexi
cesses occur
phenomena :

1) The poly
   tions of
   dependin
   fixing sta
   above the
   cessible t
   amorpho
   of stress
   ing medi
   fused int
   and, thus
2) In the dy
   number c
   gle mole
   These in
   Dissol
   Possib
   Adsor
   Assoc
   Incorp
   celles

uor

MEYER and KAR-
studies of VICK-
g of the 1950s, a
een published on
cs of dyeing cel-
ers with disperse
survey, see [315,
as well as acid
ularly dispersed
t be dissolved in
dsorb to the fiber
e fiber.
disperse dye is
sive for the dye-
y and rate of dis-
y factors includ-

rsing agent used
ration, aggrega-

disperse dyes is
creases strongly
reased manifold

er is often com-
, the thermody-
lisperse dye bet-
ie Nernst distri-

At constant temperature, the distribution coefficient K [i.e., the ratio of the concentration of dye dissolved in the fiber (C_F) and in the liquor (C_L) at equilibrium] is constant.

At normal dyeing temperatures the rate of dissolution of dispersed dyes in the dye liquor is assumed to be high, so that C_L is constant as long as undissolved dye is present. Although not always valid in practice, the motion of the liquor is also assumed to be high enough so that molecularly dissolved dye is always transported to the fiber surface in sufficient amounts and the adsorption of dye proceeds rapidly. Then, diffusion in the fiber is the step that determines the rate of dyeing. The amount of dye g that diffuses in a certain time follows Fick's first law:

$$g = -\frac{D}{h} \cdot (C_L - C_F)$$

The diffusion coefficient D is 10^{-10} to 10^{-12} cm^2/s and can be increased only by an increase in temperature. The diffusion path h is predetermined by fiber geometry; the concentration gradient $C_L - C_F$, by C_L.

Many experiments were carried out to develop an equation for the kinetics of dyeing. However, only approximations result because of the complexity of the fiber state and of the processes occurring in the dye liquor. The following phenomena are of special interest:

1) The polyester fiber contains varying proportions of crystalline and amorphous regions, depending on the degree of drawing and the fixing state. Only regions that are amorphous above the glass transition temperature are accessible to dye diffusion. During dyeing, the amorphous portion can change as a function of stress and shrinkage. In addition, the dyeing medium (water) and the dye already diffused into the fiber change the fiber structure and, thus, the dyeability.

2) In the dyebath, the dye goes through a large number of stages, from solid particle to a single molecule, which interact with each other. These include:
　　Dissolving in the liquor
　　Possibly melting
　　Adsorption of dispersing agent
　　Association to dispersing agent
　　Incorporation into dispersing agent micelles

　　Diffusion through the laminar liquor layer on the fiber surface
　　Adsorption to the fiber
　　Agglomeration, aggregation, crystal growth
　　Mutual influencing of dyes, isomorphism of different dyes (formation of mixed crystals with different solution behavior than pure components)
　　Chemical changes (e.g., reductive destruction)

3) The levelness of dyeing – the basic requirement of coloring – is endangered by differences in temperature and concentration. In practice, such differences are unavoidable because of irregularities in the velocity and direction of the liquor flow at various positions in the dyeing aggregate and gradual depletion of dye in the liquor during passage through the dyebath. Hence, a constant supply of dye at the fiber surface is not guaranteed, and diffusion no longer determines the rate of dyeing.

For this reason, the practical dyeing process cannot (yet) be described by simple theoretical models. Despite many careful studies of model systems and individual processes, which permit a semiquantitative interpretation of individual steps under standardized conditions, dyeing results still cannot be mathematically predicted unambiguously. Thus, a dyeing process must be elaborated from dyeing experiments. Recipes are drawn up on the basis of trial dyeings with the help of color measurements.

When elaborating a dyeing process in practice, it is important to realize that, with regard to the rate of absorption, the system consisting of hydrophobic fiber and disperse dye occupies an intermediate position compared to other classes of dyes. The rate of diffusion of disperse dyes into hydrophobic fibers is moderately temperature dependent. Absorption can be easily regulated by controlling the temperature. Furthermore, this intermediate position between fast and slowly diffusing dyes is characterized by adequate migration capacity of the dyes, especially at high temperature. Thus, unlevel dyeings can be leveled out within manageable periods of time. Both methods (temperature control during exhaustion and high temperature leveling)